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Clay-mediated cyclooligomerization of olefin oxides: a one-pot route to crown ethers

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Abstract

The catalytic synthesis of substituted 1,3-dioxolanes, 1,4-dioxanes, 9-crown-3, 12-crown-4 and 15-crown-5 ethers, from alkyl oxiranes and a montmorillonite type clay is discussed.

Keywords: Epoxides; Dioxolanes; Dioxanes; Crown ethers; Heterogeneous catalysis; Cyclooligomerization

Recently we have reported a very active bentonite clay[1] as a versatile Lewis–Brönsted catalyst with a great capacity to induce carbocation chemistry [1]. Also, our research group has published reports describing important features of specific ring opening reactions of epoxides with the catalyst, giving stereo and region selective vicinal *trans*-1,2-diols or alkyl cellosolves when dry n-alcohols were used as reagents [2]. The preparation of crown ethers is generally achieved stepwise by cyclic oligomerization of alkylene oxides [3] catalyzed with acids, affording low yields (38%) after tedious experimental work-up.

Now we report that the heterogeneous catalyzed reaction can be applied in the synthesis of alkyl substituted cyclic ethers under mild conditions. Thus, a simple treatment of a benzene solution (12 ml) of propylene oxide (0.06 mol) under N_2 reacted with bentonite-clay (0.25 g) during 3 h at 150°C in a 45 ml stainless steel Parr reactor model T-316 afforded crown ethers. The suspension was allowed to stand at room temperature, filtered over celite to remove the catalyst and the filtrate analyzed by GC[2].

Part of the solution was concentrated under reduced pressure and purified by column chro-

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[1] On examination by X-ray fluorescence, the montmorillonite type clay employed in this study proved to have the following composition (in %): SiO_2, 75.4; Al_2O_3, 9.3; MgO, 0.4; Fe_2O_3, 1.3; CaO, 4.0; K_2O, 0.4; TiO_2, 0.4; H_2O (110°C) 9.5. The commercial acid-activated material was obtained from Tonsil Mexicana and analyzed with a Phillips spectrometer using Cr primary radiation. The measured specific surface area was 307 m^2/g (BET N_2) and the pore volume was 0.4789 cm^3/g. The acidity by NH_3 thermodesorption was 0.099 meq/g. The particle size was 325 mesh.

[2] All compounds were analyzed with an Hewlett Packard 5890 Chromatograph with a flame ionization detector and a 20 m×0.2 mm glass capillary column packed with 5% phenyl methyl silicon. The product characterization was made by GC–MS on a Hewlett Packard 5895 spectrometer; FAB-MS were obtained in a Jeol JMA-Sx102, using positive ion mode technics. The target was bombarded with 10 KeV Xe atoms using nitrobenzyl alcohol as the matrix.

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Table 1
Influence of the epoxide substituents on the cyclooligomerization reaction[a]

Isolated product %	Ethylene oxide	Propylene oxide	Butylene oxide	Styrene oxide	Epichlorohydrin	Epibromohydrin
Substrate	2.8	16.2	13.3	34.3	94.4	91.7
Dioxolanes	29.7	31.1	23.8	52.9	2.7	3.8
Dioxanes	64.4	17.9	9.5	12.6	3.1	4.4
Trimers	0.8	3.3	2.0	–	–	–
Tetramers	2.3	29.8	42.1	–	–	–
Pentamers	–	1.4	9.4	–	–	–

[a] Epoxide 0.06 mol; clay 0.25 g; benzene 12 ml; reaction time 3 h; temperature 150°C.

matography on silica gel using n-hexane with increasing amounts of EtOAc as eluent. The fraction which contains the tetramer was purified yielding 29.8% of an oil characterized by spectroscopic means and compared with reported data [4]. ^{1}H NMR ($CDCl_3$ 300 MHz) 1.07 (d, 3H, $J=6$ Hz), 3.44 (m, 3H); MS 233($M^+ + 1$): 175(4), 157(3), 99(23), 59(100), 57(30), 41(28).

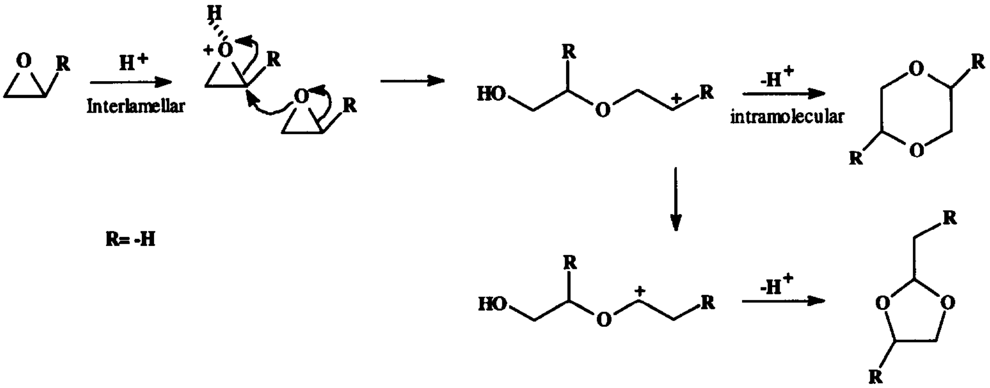
The results obtained when the reaction was performed with a related group of substituted epoxides are given in Table 1. As we can see, a larger cyclooligomerization is favoured when methyl or ethyl groups are attached to the oxirane ring, whereas bromine, chlorine or phenyl groups impedes the crown ether formation.

The negligible catalytic activity of the bentonite over epoxides supporting halogens, phenyl or alkyl–glycidil ethers should also be noted. On the other hand the aromatic ring of the styrene oxide restrains the catalyst activity mainly to the formation of dioxolanes.

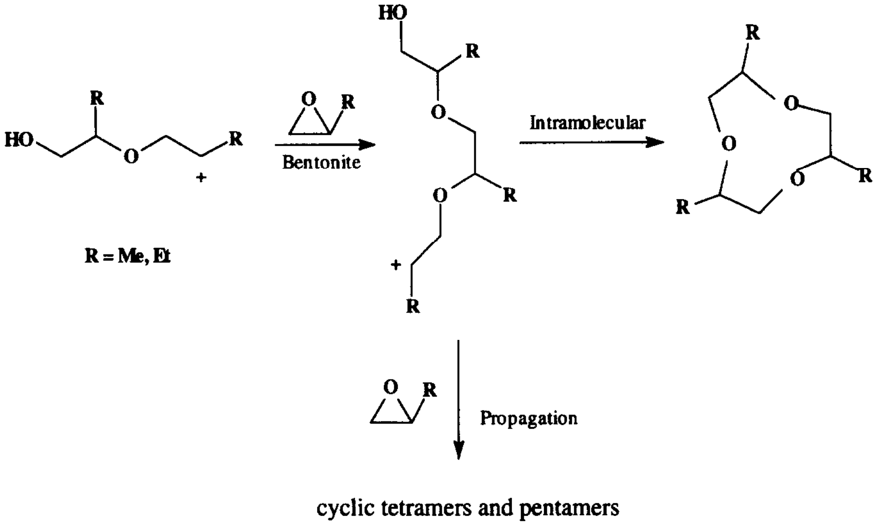
The formation of 1,4-dioxane and 1,3-dioxolane by an intramolecular coupling pathway, is in agreement with that reported by Ballantaine [5] about the dimerization of ethylene oxide with montmorillonite by means of a primary carbocation intermediate which through the hydrogen shift yield the more stable secondary species (Scheme 1).

In order to understand the genesis of larger cyclooligomers from propylene and butylene oxides promoted by the active surface, we proposed the following mechanism for the propagation reaction and the crown ether formation (Scheme 2).

The annulation by means of the carbocation species is possible due to the preferred conformation of the C–C bond in –O–CHR–CH_2–O– which adopt an helical arrangement (Gauche effect) [6] to furnish the reactive centers in a favourable disposition for cyclization. This is supported by the low activation energy value of 3.0 kcal/mol found for the propylene oxide



Scheme 1.



Scheme 2.

cyclotetramerization compared with the higher of 7.4 and 7.6 kcal/mol calculated for the dioxane and dioxolane formation. Whereas in the case of hindered epoxides like styrene oxides, halohydrines, alkyl or phenyl glycidines with bulky groups, the molecular concentration into the lamellar space of the catalyst and substrate activation is restrained.

In order to evaluate the catalytic capability, the clay was recycled four times with fresh substrate. We found a lack in the oligomer selectivity yielding 1,3-dioxolanes as the main product, suggesting the exhaustion of the lamellar interstices. Thus we can infer that this catalytic reaction proceeds through an carbocation type intermediate where its stability can be reached by two competitive pathways either by an intermolecular or by an intramolecular attack.

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