Synthesis of fatty ketoesters by tandem epoxidation-rearrangement with heterogeneous catalysis

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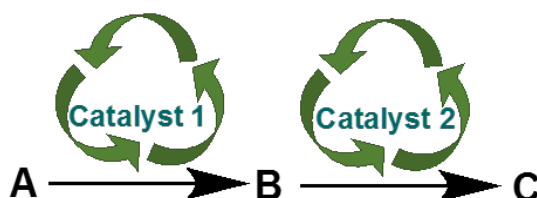
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Abstract

Unsaturated fatty esters can be easily transformed into ketoesters through a two-step process. The highly efficient epoxidation is carried out with *tert*-butyl hydroperoxide (TBHP) in α,α,α-trifluorotoluene (TFT) using a Ti-silica heterogeneous catalyst. The formed epoxide is easily rearranged by a heterogeneous Brønsted acid, with nafion-silica SAC-13 as the most efficient one. Both reactions can be combined in a tandem process, with separation of the Ti-silica catalyst by filtration from the reaction medium and addition of the second acid catalyst to perform the second reaction. Each catalyst is separated individually and can be reused, with or without re-activation, under the same conditions to maximize the productivity.

Introduction

The use of renewable raw materials, which must reduce the dependence on the fossil resources with a lower CO_2 footprint of the chemical industry, is one of the most important principles of Green Chemistry.[1] Catalysis, another important principle of Green Chemistry, should play a very important role in the transformation of the renewable materials into useful compounds.[2] Moreover, the combination of several reactions in tandem processes (Scheme 1) should help to improve the efficiency of those transformations.[3]

Scheme 1. Schematic representation of a tandem process.

Fatty esters are among the most useful raw materials,[4,5] which can be converted into compounds acting as biolubricants,[6–9] biosurfactants,[10,11] biopolymers[12,13] and many other applications. Although reactions on the ester group are the most common in oleochemical industry, the reactivity of the unsaturated hydrocarbon chains opens the way to a large variety of compounds.[14–16] Fatty ketoesters[17] are however rather unexplored as platform molecules, in spite of possessing countless synthetic possibilities. 12-Ketostearate has been obtained from ricinoleate by simultaneous hydrogenation-dehydrogenation.[18] On the other hand, mixtures of 9- and 10-ketostearates can be obtained from the oxidation of oleate. Apart from the use of bacteria for the enzymatic oxidation,[19] the direct oxidation of oleate to ketostearates has been described in a catalyst-free method using N_2O as an oxidant at high temperature (220°C) and pressure (4 MPa).[20] Alternatively, the ketostearate has been obtained by the Pd-catalyzed Wacker oxidation of oleate with oxygen. In the first examples, high amount of $PdCl_2$ (10 mol%) and CuCl (50 mol%) as co-catalysts were employed with 1 bar O_2.[21] Molecular oxygen and CuCl co-catalyst can be substituted by benzoquinone and HBF_4, together with the use of lower amount of
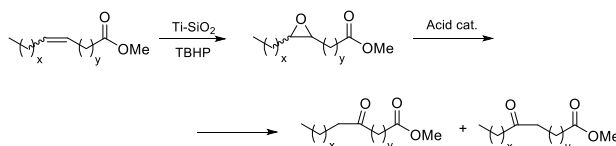
palladium catalyst (5 mol% of Pd(OAc)$_2$).[22] The use of high pressure (10 bar) of oxygen also avoids the need for a co-catalyst when the reaction is carried out in dimethylacetamide, which also allows the recovery and reuse of PdCl$_2$ catalyst.[23]

The other possibility is the two-step process of oleate epoxidation and Meinwald rearrangement of the epoxystearate to obtain the mixture of ketostearates.

The epoxidation of oleates by different procedures has been described in the literature.[24] Some of them are performed in aqueous or aqueous/organic biphasic media, such as those using H$_2$O$_2$ or oxone as an oxidant. These methods do not seem to be adequate for a tandem process with an acid-catalyzed rearrangement due to the probable epoxide ring opening to diol. In some cases molecular oxygen has been used as an oxidant in the presence of a sacrificial reagent, either an aldehyde[25] or cumene.[26] Under such conditions, at least part of the reaction takes place through a radical mechanism, leading to mixtures of *trans* and *cis* epoxides. The most efficient method for stereospecific epoxidation in anhydrous medium with heterogeneous catalysis seems to be the use of alkyl hydroperoxides, such as *tert*-butyl hydroperoxide (TBHP), in combination with Ti catalysts. The grafting of Ti sites on silica supports leads to active catalysts for epoxidation of fatty acid methyl esters, with higher activity in the case of the structured mesoporous Ti-MCM-41.[27] However, amorphous Ti-SiO$_2$ catalysts have also shown interesting features, such as higher activity per exposed Ti site.[28] More recently a sponge-like hierarchical titanium silicalite has been also described as catalyst for the epoxidation of methyl oleate.[29]

With respect to rearrangement of epoxystearate, not many examples have been described in the literature. Conventional Lewis acids, such as BF$_3$,[17] and less common ones, such as Bi(OTf)$_3$[30] and YCl$_3$[31], have been used for this purpose with high conversion and selectivity. On the other hand, heterogeneous sulfonic solids have been shown to be efficient Brønsted catalysts for this reaction.[32]

In this paper, we present our results on the epoxidation of unsaturated fatty esters with a heterogeneous Ti-silica catalyst and the Meinwald rearrangement of the epoxides, as well as the combination of both reactions in a tandem process (Scheme 2).

Scheme 2. Epoxidation of unsaturated fatty acid methyl esters and subsequent rearrangement in two tandem reactions.

Experimental

Preparation of the Ti-silica catalyst

10 g of pre-dried Merck 60 silica (0.063-0.200 mm particle size, surface area 512 m^2/g, pore volume 0.816 cm^3/g)[33] were treated with HNO$_3$ 1 M (300 mL) at room temperature for 3 h. The silica was thoroughly washed with water until neutral pH, and then dried successively under vacuum at 150°C overnight, at 500°C for 2 h under air and for 2 h under vacuum. In a glovebox, titanocene dichloride (Cp$_2$TiCl$_2$, 940 mg, 3.8 mmol) was added to the cold calcined silica and 170 mL of anhydrous CH$_2$Cl$_2$ were added via cannula. The mixture was stirred under Ar at room temperature for 2 h, then 8.6 mL of pyridine were added and stirring was maintained for 20 h. The resulting yellow solid was filtered, washed with CH$_2$Cl$_2$ until uncolored solution and dried under vacuum. Finally, the catalyst was calcined at 550°C under flow (80 mL/min) of Ar for 1 h and then of air for 20 h, to get a white solid.

Epoxidation reactions

The required amount of Ti-silica (15 µmol Ti) was added to a solution of methyl oleate (296.5 mg, 1 mmol) in α,α,α-trifluorotoluene (TFT, 5 mL) and the mixture was heated under reflux.

TBHP (0.28 mL of 5.5 M solution in decane, 1.5 mmol) was added and the reaction was monitored by GC. Once the reaction had finished (1 to 2 h) the catalyst was filtered off and washed with dichloromethane. The solvent and volatile compounds (TFT, *tert*-butanol, decane) were evaporated under reduced pressure to obtain the methyl *cis*-9,10-epoxystearate with 97% isolated yield, which was used without further purification.

The epoxidations of methyl elaidate (24 h of reaction), erucate and ricinoleate were carried out in the same way. In the case of methyl linoleate, the amount of TBHP was increased to 0.56 mL (3 mmol).

Rearrangement reactions

SAC-13 (58.8 mg, 10 µmol -SO$_3$H sites) was added to a solution of methyl *cis*-9,10-epoxystearate (312.5 mg, 1 mmol) and benzonitrile (42.5 mg, internal standard) in α,α,α-trifluorotoluene (TFT, 5 mL), and the mixture was heated under reflux and Ar atmosphere for 1 h. The reaction was monitored by GC. The catalyst was filtered off and washed with dichloromethane. The methyl oxostearates were obtained by evaporation of the solvent under reduced pressure, without further purification, to get 92% isolated yield.

The same method was used for the other fatty epoxides. In the case of methyl *cis,cis*-9,10:12,13-diepoxystearates, 117.6 mg of SAC-13 (20 µmol -SO$_3$H sites) were used.

Tandem processes

The required amount of Ti-silica (15 µmol Ti) was added to a solution of methyl oleate (296.5 mg, 1 mmol) in α,α,α-trifluorotoluene (TFT, 5 mL) and the mixture was heated under reflux. TBHP (0.28 mL of 5.5 M solution in decane, 1.5 mmol) was added and the full conversion was checked by GC after 2 h. The catalyst was filtered off. Then, SAC-13 (58.8 mg, 10 µmol -SO$_3$H sites) and benzonitrile (42.5 mg, internal standard) were added to the filtrate and the mixture was heated under reflux and Ar atmosphere for 1 h.
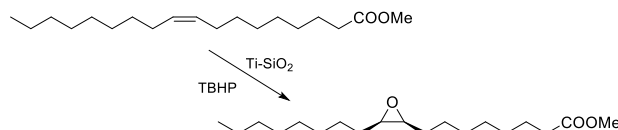
Results and discussion

Epoxidation reactions

One of the main issues about heterogeneous catalysis is the reproducibility in the preparation of the catalysts and hence their catalytic performance. In this case, Ti-silica catalyst was prepared following a procedure previously described,[34] although with some minor modifications. The silica support was treated with HNO$_3$ in order to eliminate all the traces of Fe and to prevent in this way the possible formation of radicals with the hydroperoxide. TiCp$_2$Cl$_2$ was used as the Ti precursor, and the reaction with the silanol groups on the silica surface was carried out at room temperature using pyridine as a base to favor the reaction. The solid was calcined under Ar and then air to form the final grafted Ti species and eliminate all the traces of organic matter. Along this work, 8 batches of catalyst were prepared using the same methodology, with a certain variability in the obtained Ti content, from 0.18 to 0.30 mmol/g (average 0.225 mmol/g, standard deviation 0.048). This can be due to uncontrolled slight changes in temperature and gas flow. Hence, Ti analysis is compulsory before using each batch of catalyst.

Optimization of epoxidation conditions with methyl oleate. α,α,α-Trifluorotoluene (TFT) was chosen as solvent for the epoxidation of methyl oleate (Scheme 3), given its efficiency with other substrates.[35,36] Reactions were carried out under reflux, as temperatures lower than 100°C were unable to reach quantitative conversions in short reaction times (up to 2 h). Given that Ti-silica catalysts had shown activity in the Meinwald rearrangement of aromatic epoxides,[35] the reaction was tested for a long time period in order to see the performance of this single catalyst in the two-steps one-pot process. As expected, the epoxidation reaction was fast, with total conversion after 2 h, and selective to the epoxide, whereas the catalyst showed poor activity for Meinwald rearrangement, with

only 34% selectivity to ketostearates after 1 week. This result evidences the need for a second catalyst for the rearrangement.

Scheme 3. Epoxidation of methyl oleate.

Thus, those conditions (reflux for 2 h) were kept to test the effect of the amounts of *tert*-butyl hydroperoxide (TBHP) and catalyst. The nearly stoichiometric amount of TBHP (1.1 eq) led to conversions in the range of 95-100%, irrespective from the amount of catalyst (1.2 to 2.5 mol%). The result did not show any relationship with the Ti loading of the catalyst, and hence, the amount of TBHP was increased to ensure the total conversion of methyl oleate. On the contrary, the use of 1.5 eq of TBHP was enough to get total conversion in 2 h using 1.5 mol% of Ti-silica catalyst, in reaction scales from 1 to 10 mmol of methyl oleate. Thus, these conditions of 1.5 mol% catalyst, 1.5 eq TBHP, and TFT under reflux were taken as the standard ones for the subsequent reactions.

Recovery and reuse. One important feature of the heterogeneous catalysts is the possibility of recovery and reuse of them to increase the productivity. The results with Ti-silica catalyst are represented in Figure 1. The recovered catalyst was less active than the freshly prepared one in runs 2 and 3. It required around 5 h to reach 90% conversion, and 8 h to reach 95%. However, the drop in activity was more important in the fourth run, with only 80% conversion after 8h, whereas nearly 24 h were necessary to reach 95% conversion. Then, the catalyst was reactivated by calcination after the fourth run, recovering in this way the activity shown in runs 2 and 3. Similar results were observed in run 6, with a drop in activity, and run 7, with a partial recovery of the activity after reactivation by calcination. These results indicate that there exists a deactivation mechanism due to adsorption of organic matter, which is reversible by calcination. However, another part of the activity was lost in an irreversible way. Owing to the low amount of catalyst used, it was not possible to analyze the solid after each run. However, the analysis of the catalyst after the 8th run showed a content of titanium of only 0.003 mmol/g, which implies an important loss of titanium, between 80 and 90%, responsible for the second deactivation mechanism. Taking these values, the productivity of the Ti sites after 8 runs can be estimated, considering only 90% conversion, to be around 850 mol of epoxide per mol of Ti.
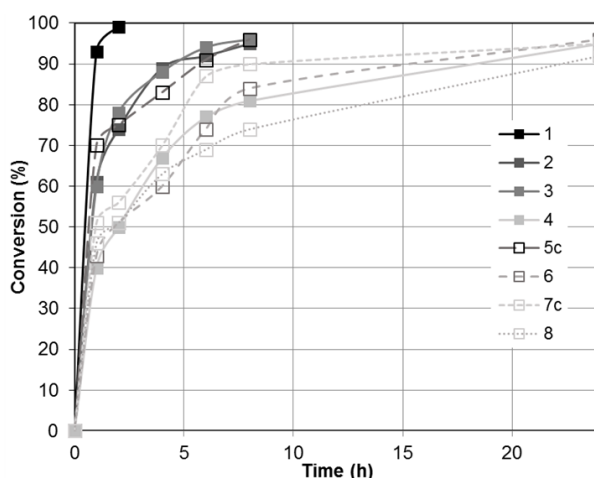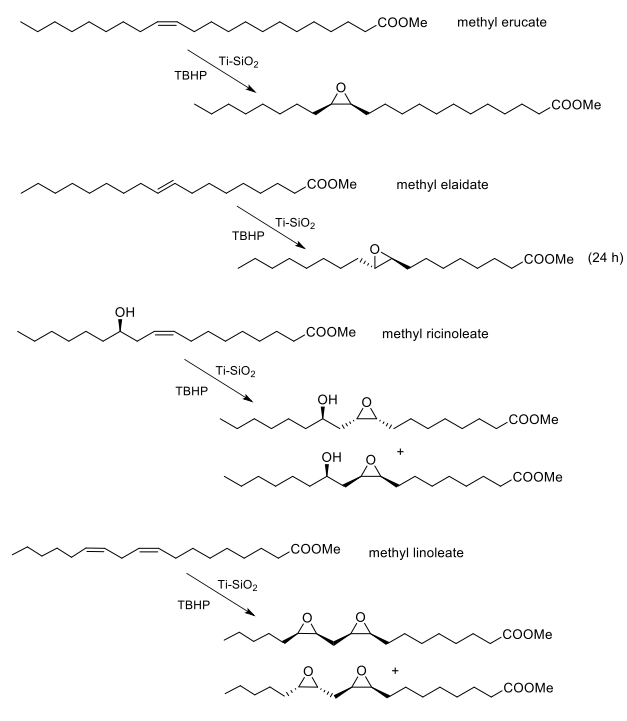

Figure 1. Reuse of Ti-silica in 8 runs of epoxidation of methyl oleate. Runs 5c and 7c were carried out after calcination of the used catalyst.

Epoxidation of other unsaturated fatty esters. The same methodology was applied to the epoxidation of four other unsaturated fatty esters (Scheme 4): one with a longer chain with *cis*

alkene (erucate, C22:1 *cis*-Δ^{13}), one with a *trans* alkene (elaidate, C18:1 *trans*-Δ^9), one with an additional functionality (ricinoleate, (R)-12-hydroxy-9-*cis*-octadecenoate) and one with two *cis* non-conjugated double bonds (linoleate, C18:2 *cis,cis*-Δ^9,Δ^{13}). Under the same conditions with oleate, the result with methyl erucate was analogous, total conversion in 2 h. However, the lower reactivity of the *trans* alkene in elaidate slows down the reaction and it takes 24 h for complete conversion. The presence of the hydroxyl group in methyl ricinoleate does not produce any modification of the reactivity, leading to total conversion in 2 h. Although only one peak in GC was detected, the formation of the two possible diastereomers in nearly equimolecular amounts was inferred by the duplicity in the signals of the ^{13}C-NMR spectrum (see Supporting Information). In the case of linoleate, it was not possible to obtain the monoepoxides selectively, even using a low amount of TBHP. The selectivity to monoepoxides was high only at very low conversions, as the diepoxides were formed even at low concentration of the monoepoxides. Double amount of oxidant was used to get full conversion to the diepoxides in only 2 h. Two peaks were detected in GC, in agreement with the two possible diastereomers that can be formed.

Scheme 4. Epoxidation of different unsaturated fatty methyl esters.

Meinwald rearrangement of fatty epoxides

Optimization with methyl cis-9,10-epoxystearate. Given that the Ti-SiO$_2$ epoxidation catalyst is not acidic enough to efficiently promote the Meinwald rearrangement of the *cis*-9,10-epoxystearate to a mixture of 9-oxo- and 10-oxostearates (Scheme 5), a variety of homogeneous Lewis as alternatives to the already described,[30,31] and heterogeneous Brønsted acid catalysts, including SAC-13[32] and other sulfonic solids, was tested with this purpose (Table 1). Regarding reaction conditions, TFT was used as solvent in most of the reactions in order to check the possibility of carrying out the two-steps process in one-pot or tandem. It is worth noting that no other products but methyl ketostearate were detected in the reaction mixtures, by either GC or NMR, indicating that the reaction has 100% selectivity to the rearrangement.

Scheme 5. Rearrangement of methyl *cis*-9,10-epoxystearate to methyl 9(10)-oxostearate.
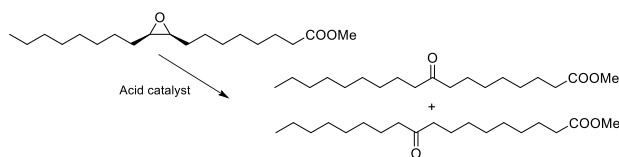

Table 1. Results of the Meinwald rearrangement of methyl *cis*-9,10-epoxystearate with different catalysts.[a]

Catalyst	mol%	Solvent	T (°C)	t (h)	Conv. (%)[b]
Homogeneous Lewis acids					
$Cu(OTf)_2$	5	TFT	120	2	>99
$Zn(OTf)_2$	5	TFT	120	2	>99
$Yb(OTf)_3$	5	TFT	120	2	>99
			80	2	>99
			50	3	>99
			30	6	>99
$Co(ClO_4)_2$	5	TFT	120	24	>99
$Zn(ClO_4)_2$	5	TFT	120	24	91
Heterogeneous Brønsted acids					
K10 montm.	5	TFT	120	24	41
Deloxan	5	TFT	120	24	>99
			80	24	96
		Toluene	120	3	>99
		PhCl	140	3	>99
		DMF	160	7	7
Amberlyst 15	5	TFT	120	24	74
Dowex 50W×2	5	TFT	120	24	>99
Nafion NR-50	5	TFT	120	2	>99
SAC-13	5	TFT	120	2	>99
SAC-13	2	TFT	120	2	>99
SAC-13	1	TFT	120	1	>99
		TFT	50	3	>99
		TFT	30	24	>99
		Toluene	120	1	>99
		PhCl	140	1	>99
		DMF	160	7	5
Aquivion	5	TFT	120	1	>99
PW79S	1	TFT	120	1	>99
Aquivion P98	5	TFT	120	8	99

[a] Scale: epoxide (1 mmol), solvent (5 mL). [b] Determined by gas chromatography.

As can be seen, all the homogeneous Lewis acids (5 mol%) led to conversions over 90%, with triflates as the most efficient ones, irrespective from the metal used (copper, zinc, ytterbium), whereas with perchlorates the reaction required 24 h to reach similar conversion values. With $Yb(OTf)_3$ it was shown that the reaction also is efficient at lower temperatures, although below 50°C the reaction is slightly slower.
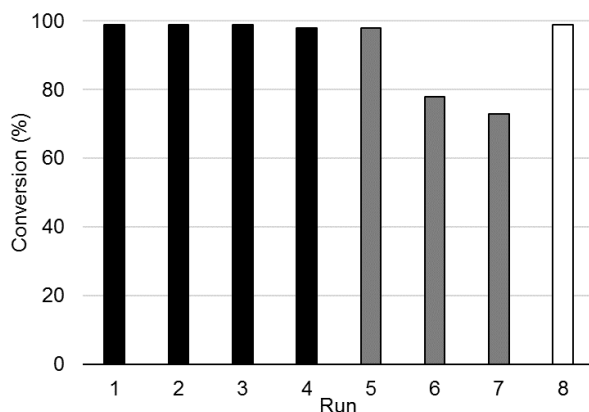
Regarding the heterogeneous Brønsted acid catalysts, the acidic K10 montmorillonite was not efficient, with only 41% conversion after 24 h. Thus, sulfonic solids with sites of different strength were tested: *i*) Deloxan (alkylsulfonic polysiloxane); *ii*) Amberlyst 15 and Dowex 50W×2 (arylsulfonic poly(styrene-divinylbenzene) resins); *iii*) Nafion, SAC-13 (nafion-silica composite) and Aquivion (perfluoroalkylsulfonic resins). All of them were active at 120°C, although the strongest perfluoroalkylsulfonic resins were much more efficient than the other weaker sulfonic solids, as it had been already described by Ríos *et al* in the comparison of SAC-13 and Amberlyst 15.[32]

The cross-linking degree was important in the case of poly(styrene-divinylbenzene) resins, and the gel type Dowex 50W×2, with only 2% cross-linking agent, was more efficient than the macroreticular Amberlyst 15, with 20% cross-linking divinylbenzene. This effect has been already observed in other reactions catalyzed by this kind of solids,[37,38] and it has been ascribed to accessibility problems to some of the sulfonic sites in the inner part of the resin, which is probably the reason for the poor results previously described with this catalyst.[32]

Regarding the perfluoroalkylsulfonic resins, both Nafion and Aquivion PW79S performed similarly, with total conversion after 2 h, as well as the nafion-silica composite SAC-13. Due to the problems found in the filtration of Aquivion PW79S (powder), another analogous catalyst in the form of pellets was prepared from Aquivion P98 by hydrolysis[39] (see Supporting Information). However, the efficiency of this solid was lower, probably by accessibility problems, as pointed for Amberlyst 15. SAC-13 was considered as the most convenient catalyst and, in fact, it was possible to decrease the amount of catalyst from 5 mol% to only 1 mol% with the same results, reaching total conversion in only 1 h.
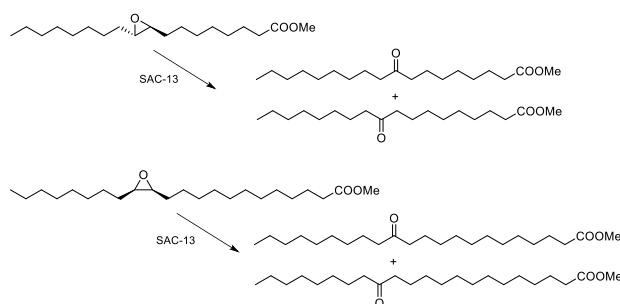
The effect of solvent and temperature was checked with Deloxan (5 mol%) and SAC-13 (1 mol%). As observed in the case of homogeneous Lewis acids, the heterogeneous Brønsted acids can also promote the rearrangement at lower temperature, although it was slower, in agreement with results described in the literature.[32] Non-polar solvents, such as toluene or chlorobenzene, were suitable for this reaction, but a polar solvent, such as dimethylformamide, produced the deactivation of the catalyst, probably because its weak basicity. Anyway, TFT under reflux (120 °C) was the solvent and temperature of choice to make compatible both epoxidation and Meinwald rearrangement.

Figure 2. Reuse of SAC-13 (1 mol%) in the Meinwald rearrangement of methyl *cis*-9,10-epoxystearate. Black bars: results in 1 h. Grey bars: results in 2 h. White bar: result in 2 h after treatment of the catalyst with HCl.

Recovery of SAC-13 in the Meinwald rearrangement. The possibility of recycling and reuse was checked in the case of SAC-13. As can be seen in Figure 2, the catalyst kept its activity in four consecutive runs, with a slight drop in activity in the fifth one (2 h required for total conversion). The deactivation was more important in the two subsequent runs, but it was possible to regenerate the catalyst by treatment with HCl.
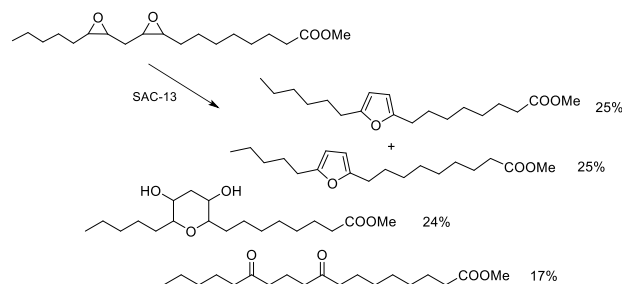
Meinwald rearrangement of different fatty epoxides. The same methodology, SAC-13 1 mol% in TFT under reflux, was applied to the other prepared epoxides. The simple epoxides (Scheme 6), methyl *trans*-9,10-epoxystearate and *cis*-13,14-epoxydocosanoate (or epoxybehenate) led to the expected ketones with total conversion in 2 h, showing no effect of the stereochemistry of the oxirane ring.

Scheme 6. Rearrangement of methyl *trans*-9,10-epoxystearate and *cis*-13,14-epoxydocosanoate.
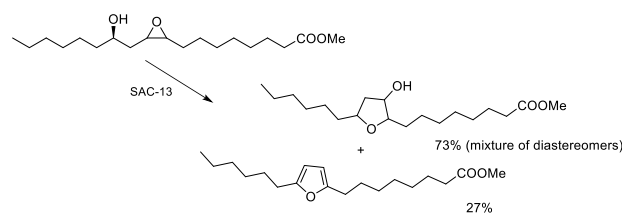
On the contrary, the epoxides with additional functionalization led to complex mixtures of products, which were separated by column chromatography on silica and characterized by NMR. The rearrangement of methyl *cis,cis*-9,10:12,13-diepoxystearates (Scheme 7) produced 50% yield of furanic fatty esters, with furan in positions (9,12) and (10,13). These products had been already described as the only ones obtained in early attempts of Meinwald rearrangements,[40] and more recently as by-products in the ring opening with alcohols catalyzed by either Amberlyst 15 or H_2SO_4.[41] Besides the furanic fatty esters, 24% yield of 3,5-dihydroxytetrahydropyrans was also obtained. This type of products had been proposed, on the basis on mass spectra of TMS derivatives, as products in the reaction of the *threo* isomer of methyl *cis,cis*-9,10:12,13-diepoxystearate with acetic or trichloroacetic acids,[42] although they had not been isolated and fully identified to the best of our knowledge. Moreover, 17% yield of methyl 9,13-dioxostearate (1,5-diketone) was also obtained. The remaining 9% yield corresponds to a complex mixture of tetrahydrofuranic derivatives, although they could not be separated in pure form and unequivocally identified.

Scheme 7. Rearrangement and cyclization of methyl *cis,cis*-9,10:12,13-diepoxystearates catalyzed by SAC-13.

The treatment of methyl *cis*-9,10-epoxy-12-hydroxystearates with a Brønsted acid (Scheme 8) promotes the intramolecular attack of the protonated epoxide by the hydroxyl group, leading to

a 3-hydroxytetrahydrofuran structure. Cyclizations leading to hydroxytetrahydrofurans had been reported in the acid catalyzed ring opening of linoleate diepoxide,[43,44] and in its biocatalytic rearrangement.[45] The formation of tetrahydrofurans without hydroxyl group had been also described in the functionalization of ricinoleate by oxymercuriation-demercuriation.[46] However, the presence of the aromatic furan was rather unexpected. It seems that the strong Brønsted acid is able to dehydrate the hydroxytetrahydrofuran to dihydrofuran, which is finally aromatized in a process through an unknown mechanism.

Scheme 8. Cyclization of methyl *cis*-9,10-epoxy-12-hydroxystearates catalyzed by SAC-13.

One-pot and tandem processes

The sequence of the two reactions was first tested with methyl oleate in one-pot, by addition of all the components (oxidant, Ti-silica catalyst and SAC-13 acid catalyst) to the reaction mixture from the beginning. After 2 h, only 23% conversion was observed, 19% to oxostearate, much lower than in the sequence of the two single reactions. After 48 h the conversion only increased to 65%, but due to the isomerization of the *cis* double bond of oleate with the strong acid catalyst to the most stable *trans* double bond of methyl elaidate. The detected problem was the decomposition of TBHP in the presence of a strong Brønsted acid, given that further additions of TBHP made the reaction progress until total conversion to oxostearate with a total amount of 4.5 eq of TBHP added into three portions of 1.5 eq at reaction times of 0, 1 and 2 h. In fact, the same effect can be obtained by addition of the acid catalyst after the epoxidation reaction has finished. However, with this system, the advantage of the one-pot method (just putting all the components from the beginning) is lost and both catalysts are recovered as a mixture at the end of the reaction, without possibility of reuse under the same conditions.

Thus, it would be advantageous the use of the tandem procedure,[47,48] that is the filtration of the Ti-silica catalyst at the end of the first reaction and then addition of SAC-13 to perform the second one. In this way, total conversion to oxostearate is obtained in a total reaction time of 3 h (2 + 1), with 90% isolated yield, and each catalyst can be recovered and reused with or without reactivation, in a similar way to the single reactions, to reach its optimal productivity.

Conclusions

The optimization of the reactions of epoxidation of unsaturated fatty esters and subsequent Meinwald rearrangement, in the same solvent, has allowed the combination and compatibilization of both reactions in a tandem process (90% yield in oxostearates) improving the results obtained in one-pot (20% yield). Moreover, this tandem strategy uses the reaction crude, without intermediate steps of separation and purification; hence, a sustainability improvement of the overall process has been achieved. In addition, in this way, the use of each catalyst can be optimized increasing the productivity of both catalysts individually. Ti-catalyst can be reused during 4 cycles and SAC-13 during 7 cycles before their independent reactivation, through calcination and HCl treatment respectively.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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